Photochemistry of the Venus Atmosphere

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ABSTRACT

Carbon monoxide, produced in the Venus atmosphere by photolysis of CO_2, is removed mainly by reaction with OH. The radical OH is formed in part by photolysis of H_2O_2, in part by reaction of O with HO_2. Photolysis of HCl provides a major source of H radicals near the visible clouds of Venus and plays a major role in the overall photochemistry. The mixing ratio of O_2 is estimated to be approximately 10^{-7}, about a factor of 10 less than a recent observational upper limit reported by Traub and Carleton. A detailed model, which accounts for the photochemical stability of Venus CO_2, is presented and discussed.

1. Introduction

The atmosphere of Venus is composed primarily of CO_2, but contains detectable trace quantities of CO, H_2O, HCl and HF. Carbon dioxide is dissociated readily by sunlight at wavelengths <2000 Å, and the observed abundance of CO, approximately 5×10^{-5} that of CO_2, could be produced photochemically in as little as 200 years. Similar remarks apply to O_2. Spectroscopic observations by Traub and Carleton (1973) suggest an upper limit to the O_2 mixing ratio of about 10^{-6}, and an abundance in excess of this limit could be formed photochemically in less than 10 years. Our present task is to account for the stability of CO_2 in the atmosphere of Venus and, in so doing, to provide an explanation for the remarkable deficiency of CO and O_2.

A similar problem has arisen for Mars and was treated recently by McElroy and Donahue (1972) and by Parkinson and Hunten (1972). It appears that recombination of CO_2 in the Martian atmosphere is catalyzed by trace quantities of H and OH, produced by photolysis of H_2O. Removal of CO proceeds by two main paths:

$$\left.\begin{aligned} H+O_2+CO_2 &\rightarrow HO_2+CO_2 \\ O+HO_2 &\rightarrow OH+O_2 \\ CO+OH &\rightarrow CO_2+H \end{aligned}\right\}, \tag{1}$$

and

$$\left.\begin{aligned} 2[H+O_2+CO_2 &\rightarrow HO_2+CO_2] \\ 2HO_2 &\rightarrow H_2O_2+O_2 \\ h\nu+H_2O_2 &\rightarrow 2OH \\ 2[CO+OH &\rightarrow CO_2+H] \end{aligned}\right\}. \tag{2}$$

The first corresponds to the net reaction

$$H+CO+O \rightarrow H+CO_2, \tag{1'}$$

and the second is equivalent to

$$2H+2CO+O_2 \rightarrow 2H+2CO_2. \tag{2'}$$

We shall argue here that recombination of CO_2 in the atmosphere of Venus proceeds by a combination of (1) and (2). The necessary source of H is provided by

$$h\nu+HCl \rightarrow H+Cl, \tag{3}$$

followed by

$$Cl+H_2 \rightarrow HCl+H. \tag{4}$$

Reactions (3) and (4) lead to net dissociation of H_2, the rate of which can be estimated if the concentration of HCl is taken as given.

2. Assumptions and general approach

Using the observed mixing ratio of HCl, about 6×10^{-7} according to Connes *et al.* (1967), we estimate a global mean rate for production of H atoms by (3) and (4) equal to 4×10^{11} cm^{-2} sec^{-1}. The corresponding rate for destruction of H_2 is 2×10^{11} cm^{-2} sec^{-1} and must be balanced by a source of comparable magnitude. As we shall see, the necessary H_2 source is provided in part by

$$H+HO_2 \rightarrow H_2+O_2, \tag{5}$$

with an additional contribution from the global reaction

$$CO+H_2O \rightarrow CO_2+H_2. \tag{6}$$

Reaction (5) occurs primarily above the visible cloud tops, where the atmospheric pressure is about 0.2 atm and the temperature about 250K. Reaction (6) occurs mainly in the deep atmosphere, near the surface, where the pressure is about 95 atm and the temperature about 750K.

We shall assume that CO in the atmosphere of Venus is produced primarily by photolysis of CO_2. We assume further that CO is mixed uniformly throughout the atmosphere. The total abundance of CO is then about 10^{23} molecules cm^{-2} and there must be a comparable

amount of free oxygen. Our model should account for this oxygen reservoir. The observations of Traub and Carleton (1973) seem to rule out O_2 as the major component of the reservoir. A more likely candidate is water, formed by the reaction sequence

$$\left.\begin{aligned} h\nu + HCl &\rightarrow H + Cl \\ Cl + H_2 &\rightarrow HCl + H \\ 2[H + O_2 + CO_2 &\rightarrow HO_2 + CO_2] \\ 2HO_2 &\rightarrow H_2O_2 + O_2 \\ h\nu + H_2O_2 &\rightarrow 2OH \\ CO + OH &\rightarrow CO_2 + H \\ H + O_2 + CO_2 &\rightarrow HO_2 + CO_2 \\ OH + HO_2 &\rightarrow H_2O + O_2 \end{aligned}\right\}, \tag{7}$$

for which the equivalent stoichiometric equation is

$$H_2 + O_2 + CO \rightarrow H_2O + CO_2. \tag{7'}$$

Our detailed models assume, therefore, that the total abundance of H_2O must be at least as large as that of CO, i.e., that the mixing ratio of H_2O in the lower atmosphere must be 5×10^{-5} or larger. This assumption is consistent with, but not required by, the available observational data. Reported mixing ratios for H_2O range from low values of order 10^{-6} (Young, 1972; Fink *et al.*, 1972) to high values of order 10^{-2} (Avduevsky *et al.*, 1970; Vinogradov *et al.*, 1971). The low values are associated with infrared spectroscopic studies which emphasize conditions near or above the visible cloud deck. The highest mixing ratios were detected by Venera probes and refer to conditions near the 1-atm pressure level. It is clear, however, from recent studies of the Venus emission spectrum at radio wavelengths (Janssen *et al.*, 1973) that the Venera measurements cannot represent planetary mean conditions. The average mixing ratio of H_2O must be less than 2×10^{-3} at pressure levels of about 2 atm (Janssen *et al.*, 1973). Radio (Berge and Greisen, 1969; Sinclair *et al.*, 1972) and radar (Rogers *et al.*, 1972) data would permit, but do not require, larger mixing ratios, $\sim5\times10^{-3}$, at lower atmospheric levels.

In view of the present uncertainties regarding the abundance and height distribution of Venus H_2O, we propose here to consider two distinct models, one dry, one wet. The dry model assumes that the mixing ratio of H_2O in the stratosphere may be significantly less than that in the lower atmosphere. This result could hold if H_2O were a major component of the Venus clouds. It would be appropriate, in particular, if the main clouds were composed of H_2SO_4 as suggested recently by Young (1973). The wet model assumes that the stratospheric mixing ratio is the same as the mixing ratio in the lower atmosphere. The wet model, as implied earlier, is constrained to give a H_2O mixing ratio greater than or equal to that of CO at all heights.

Water formed by reactions (7) must be removed elsewhere at an equivalent rate. In the models discussed here, removal of H_2O occurs in the upper atmosphere by photolysis followed by

$$\left.\begin{aligned} CO + OH &\rightarrow CO_2 + H \\ H + O_2 + CO_2 &\rightarrow HO_2 + CO_2 \\ H + HO_2 &\rightarrow H_2 + O_2 \end{aligned}\right\}, \tag{8}$$

with additional loss in the lower atmosphere associated with reaction (6).

The strategy adopted for this work is as follows. We assume that CO, O_2, HCl, H_2 and H_2O are mixed homogeneously with CO_2, at least above the visible cloud deck. We assume further that the abundances of odd hydrogen, odd oxygen and free chlorine are given by photochemical equilibrium. For present purposes H, OH, HO_2 and H_2O_2 are considered as odd hydrogen; O, OH and O_3 as odd oxygen; and Cl and Cl_2 as free chlorine.

The assumption of photochemical equilibrium for odd H is equivalent (see Appendix A) to the statement

$$p(H_2) + p(H_2O) = 0, \tag{9}$$

where $p(i)$ denotes the net rate for production of species i at height z. Similarly, photochemical equilibrium for odd O and free chlorine requires

$$p(CO_2) + p(H_2O) + 2p(O_2) = 0, \tag{10}$$

$$p(HCl) = 0. \tag{11}$$

Acceptable physical solutions must satisfy the additional constraints

$$\int_0^\infty p(i)dZ = 0, \tag{12}$$

where i denotes CO_2, O_2, H_2O, H_2 and HCl. If we assume (9)–(11) as given, then (12) introduces an additional pair of independent constraints. If (12) is satisfied for any pair of linearly independent constituents, for example O_2 and H_2 or O_2 and CO, then Eqs. (9)–(11) ensure that (12) must be satisfied for all i.

In practice, we take the mixing ratios of HCl and H_2O as given. We then vary the mixing ratios of O_2 and CO in an attempt to satisfy the integral constraints (12) for all major species. There is, of course, no guarantee that any physically acceptable solution should exist to the problem as posed. Indeed, we find it necessary in the dry model to allow for removal of H_2O in the lower atmosphere by reaction (6). The magnitude of the downward flux of H_2O is a function of the value assumed for the rate constant for

$$OH + HO_2 \rightarrow H_2O + O_2. \tag{13}$$

Somewhat arbitrarily, we adopted a value 10^{-10} cm^3 sec^{-1} for this constant in the dry model, a factor of 2 less than that used in the wet model. It is possible in the wet model to find an acceptable solution in which height-integrated production and loss rates are in balance for all major constituents without the need to invoke lower atmospheric chemistry. Both wet and dry

TABLE 1. Height z, above the visible cloud tops, taken at a planetocentric distance of 6112 km, number density n, and temperature T for the model atmosphere.

Height (km)	Number density (cm^{-3})	Temperature (°K)
0	6.8(18)	255
2	4.2(18)	246
6	2.1(18)	232
10	1.0(18)	217
14	4.5(17)	200
18	2.0(17)	188
22	7.4(16)	180
26	2.8(16)	175
30	9.9(15)	171
39	1.0(15)	165
44	2.4(14)	183
54	1.6(13)	212
64	1.5(12)	246
74	1.8(11)	334

models provide satisfactory solutions to the overall stability problem.

The present work does not explicitly allow for atmospheric dynamics. We assumed implicitly that dynamics plays a dominent role for CO_2, CO, O_2, H_2O, H_2 and HCl, but that chemistry dominates for odd H, odd O and free Cl. In order to assess the validity of these assumptions we compute chemical time constants for major photochemically active species. It seems probable that CO, O_2, H_2O, H_2 and HCl are indeed uniformly mixed with CO_2 over the major height range of interest here. On the other hand, the assumption of photochemical equilibrium may be suspect for H, O and Cl, particularly at higher altitudes. The neglect of dynamics is unlikely, however, to introduce any major error in the present discussion. We offer a qualitative discussion of the possible effects of dynamics.

3. Chemical model

The model atmosphere adopted for present purposes is summarized in Table 1. The height scale is referred to a zero reference level near the top of the visible cloud deck, at a planetocentric distance of 6112 km. A more detailed description of the model, which was constructed on the basis of the available spacecraft data, is given elsewhere (NASA, 1972).

Solar fluxes in the visual and near-ultraviolet were taken from the *Handbook of Geophysics and Space Environments* (1965). We used data by Detwiler *et al.* (1961), as tabulated by Brinkmann *et al.* (1966), for the wavelength interval 1750–3000 Å. Below 1750 Å we used more recent observations by Widing *et al.* (1970). Absorption cross sections for CO_2, HCl and H_2O were taken from Shemansky (1972), Romand and Vodar (1948) and Thompson *et al.* (1963), respectively.

The detailed chemical model is summarized in Table 2 and the relevant photochemical equations are presented and discussed in Appendix A. For both wet and dry models, loss of odd hydrogen proceeds primarily by (5). Below 6 km, the relative concentrations of H, OH and HO_2 are controlled by k_3, k_5, k_9 and J_6. Then

$$[HO_2]=\left\{\frac{k_3[O_2][CO_2](J_5[H_2O]+J_4[HCl])}{2k_9k_{10}}\right\}^{\frac{1}{3}}, \quad (14)$$

$$[H]=\frac{2^{\frac{1}{3}}k_9^{\frac{1}{3}}}{[O_2]^{\frac{1}{3}}[CO_2]^{\frac{1}{3}}k_3^{\frac{1}{3}}k_{10}^{\frac{2}{3}}}\{J_5[H_2O]+J_4[HCl]\}^{\frac{2}{3}}, \quad (15)$$

$$[OH]=\frac{2^{\frac{1}{3}}k_3^{\frac{2}{3}}k_9^{\frac{1}{3}}[O_2]^{\frac{2}{3}}[CO_2]^{\frac{2}{3}}\{J_5[H_2O]+J_4[HCl]\}^{\frac{2}{3}}}{k_5k_{10}^{\frac{2}{3}}[CO]}. \quad (16)$$

Between 6 km and 18 km, reactions k_4 and k_{12} are more important than k_9 and J_6. In this case

$$[HO_2]=\frac{k_3[O_2][CO_2]\{J_4[HCl]+J_5[H_2O]\}}{k_{10}J_1[CO_2]}, \quad (17)$$

TABLE 2. Reactions and rate constants for Venus. Rate constants for 2- and 3-body reactions have units cm^3 sec^{-1} and cm^6 sec^{-1}, respectively. Planetary mean rates for photolysis have units sec^{-1}, and numerical values are presented for an approximate elevation of 30 km above the visible cloud deck.

Reaction		Rate	Reference
$h\nu+CO_2$	$\rightarrow CO+O$	$J_1=1\times10^{-11}$	(see text)
$h\nu+O_2$	$\rightarrow O+O$	$J_2=1\times10^{-9}$	(see text)
$h\nu+O_3$	$\rightarrow O+O_2$	$J_3=8.8\times10^{-3}$	(see text)
$h\nu+HCl$	$\rightarrow H+Cl$	$J_4=1\times10^{-7}$	(see text)
$h\nu+H_2O$	$\rightarrow OH+H$	$J_5=4\times10^{-7}$	(see text)
$h\nu+H_2O_2$	$\rightarrow OH+OH$	$J_6=1\times10^{-4}$	(see text)
$h\nu+Cl_2$	$\rightarrow Cl+Cl$	$J_7=1.3\times10^{-3}$	(see text)
$CO+O+CO_2$	$\rightarrow CO_2+CO_2$	$k_1=2\times10^{-37}$	(a)
$O+O+CO_2$	$\rightarrow O_2+CO_2$	$k_2=3\times10^{-33}\left(\frac{T}{300}\right)^{-2.9}$	(b)
$H+O_2+CO_2$	$\rightarrow HO_2+CO_2$	$k_3=2\times10^{-31}\left(\frac{T}{273}\right)^{-1.8}$	(c)
$O+HO_2$	$\rightarrow OH+O_2$	$k_4=7\times10^{-11}$	(d)
$CO+OH$	$\rightarrow CO_2+H$	$k_5=9\times10^{-13}\exp\left(-\frac{500}{T}\right)$	(e)
$H+O_3$	$\rightarrow OH+O_2$	$k_6=2.6\times10^{-11}$	(f)
$O+O_2+CO_2$	$\rightarrow O_3+CO_2$	$k_7=1.4\times10^{-33}\left(\frac{T}{300}\right)^{-2.5}$	(g)
$O+OH$	$\rightarrow O_2+H$	$k_8=5\times10^{-11}$	(f)
HO_2+HO_2	$\rightarrow H_2O_2+O_2$	$k_9=9.5\times10^{-12}$	(d)
$H+HO_2$	$\rightarrow H_2+O_2$	$k_{10}=1\times10^{-12}$	(e)
$OH+HO_2$	$\rightarrow H_2O+O_2$	$k_{11}=2\times10^{-10}$	(f)
$H+HO_2$	$\rightarrow OH+OH$	$k_{12}=3\times10^{-11}$	(h)
$H+H+CO_2$	$\rightarrow H_2+CO_2$	$k_{13}=2.6\times10^{-32}$	(i)
$Cl+H_2$	$\rightarrow HCl+H$	$k_{14}=8\times10^{-11}\exp\left(-\frac{2480}{T}\right)$	(k, m)
$Cl+Cl+CO_2$	$\rightarrow Cl_2+CO_2$	$k_{15}=2.7\times10^{-32}$	(j)

(a) Simonaites and Heicklen (1972).
(b) Reeves *et al.* (1960).
(c) Baulch *et al.* (1969).
(d) Hochanadel *et al.* (1969).
(e) McElroy and Donahue (1972).
(f) Kaufman (1964).
(g) Kaufman (1969).
(h) K. Schofield (1967).
(i) Larkin and Thrush (1964).
(j) Bader and Ogryzlo (1964).
(k) Westenberg and de Hass (1968).
(l) Dainton and Ayscough (1967).

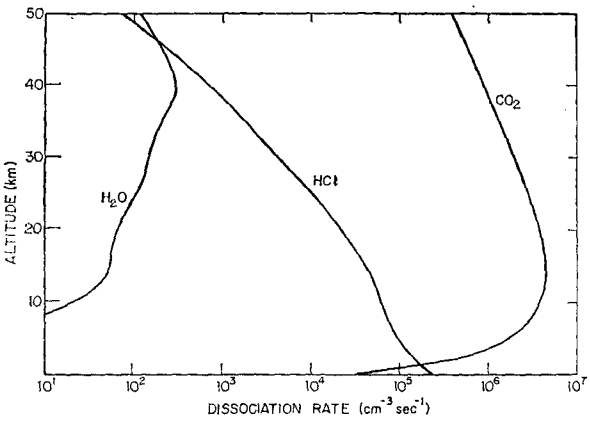

FIG. 1. Dissociation rates for H_2O, HCl and CO_2 as a function of height above the Venus cloud deck.

$$[H]=\frac{J_1[CO_2]}{k_3[O_2][CO_2]}, \tag{18}$$

$$[OH]=\frac{J_1[CO_2]}{k_5[CO]}, \tag{19}$$

$$[O]=\frac{k_{10}\{J_1[CO_2]\}^2}{k_4k_3[O_2][CO_2]\{J_4[HCl]+J_5[H_2O]\}}. \tag{20}$$

Above 20 km, OH and HO_2 are controlled by k_8 and k_4, and

$$[H]=\left\{\frac{J_4[HCl]+J_5[H_2O]}{k_{13}[CO_2]}\right\}^{\frac{1}{2}}, \tag{21}$$

$$[HO_2]=\frac{k_3[O_2][CO_2]}{k_4}\left\{\frac{2k_2(J_4[HCl]+J_5[H_2O])}{k_{13}J_1[CO_2]}\right\}^{\frac{1}{2}}, \tag{22}$$

$$[OH]=\frac{k_3[O_2][CO_2]}{k_8}\left\{\frac{2k_2(J_4[HCl]+J_5[H_2O])}{k_{13}J_1[CO_2]}\right\}^{\frac{1}{2}}, \tag{23}$$

$$[O]=\left(\frac{J_1}{2k_2}\right)^{\frac{1}{2}}. \tag{24}$$

Relations (14)–(24) hold approximately for the height ranges as indicated and provide a valuable analytic framework for interpretation of the detailed numerical results. We note in particular that the analytic results given here imply that the rate R for recombination of CO can be approximated by

$$R(CO)=2^{\frac{1}{2}}k_3^{\frac{3}{2}}k_9^{\frac{1}{2}}k_{10}^{-\frac{3}{2}}[O_2]^{\frac{3}{2}}[CO_2]^{\frac{3}{2}}\times\{J_5[H_2O]+J_4[HCl]\}^{\frac{3}{2}}, \tag{25}$$

$$R(CO)=J_1[CO_2], \tag{26}$$

$$R(CO)=\frac{k_5k_3[CO][O_2][CO_2]}{k_8}\times\left\{\frac{2k_2(J_4[HCl]+J_5[H_2O])}{k_{13}J_1[CO_2]}\right\}^{\frac{1}{2}}, \tag{27}$$

for the height ranges 0–6 km, 6–18 km, and above 20 km respectively. Recombination of CO takes place primarily below 20 km. Both (1) and (2) are important and the height-integrated rate for recombination of CO varies approximately as $f_{O_2}^{0.6}$ where f_{O_2} is the mixing ratio of O_2. It is interesting to note that the height-integrated rate for recombination of CO is essentially independent of f_{O_2} if loss of odd hydrogen proceeds mainly by (13) (see Appendix A), in which case H_2 cannot be conserved.

The relative rates for production of H_2O and H_2 depend on the abundances of OH and H. Most of the H_2O is formed below 5 km where the formation rate is given by

$$R(H_2O)=\frac{k_3k_{11}[O_2][CO_2]\{J_5[H_2O]+J_4[HCl]\}}{k_5k_{10}[CO]}. \tag{28}$$

The height-integrated rate for production of H_2O is thus directly proportional to $k_{11}f_{O_2}$ and inversely proportional to $k_{10}f_{CO}$.

Dissociation of CO_2 above 20 km is followed by production of O_2, which is transported to lower altitudes and removed mainly by (2). Approximately half the oxygen formed by photolysis of CO_2 recombines by (1), the remainder by (2).

4. Results

Figure 1 shows planetary mean rates for photodissociation of CO_2, HCl and H_2O. These results were obtained with the dry atmospheric model in which the mixing ratios of HCl and H_2O are 7.5×10^{-7} and 1.0×10^{-6}, respectively. The atmospheric capacity is due primarily to CO_2, and results for H_2O and HCl can be readily scaled to allow for different mixing ratios of these species. In particular, dissociation rates for H_2O in the wet model, for which the H_2O mixing ratio is 5×10^{-5}, are simply obtained by multiplying the relevant data in Fig. 1 by a factor of 50. Effects of cloud opacity were not explicitly considered in the present calculations but are not expected to seriously modify the conclusions.

The results shown here differ in at least one important respect from calculations presented earlier by Prinn (1971). We note that dissociation of CO_2 is significant at all altitudes in Fig. 1. In contrast, Prinn's analysis assumed that dissociation of CO_2 should be negligible below 20 km. The discrepancy is attributed to differences in the choice of absorption cross section for CO_2. Prinn (1971) used data summarized by Schultz and Holland (1963) and treated only absorption at wavelengths <1975 Å. The present analysis uses Shemansky's more recent cross sections (1972). We assumed that the quantum yield from CO_2 photolysis was unity at wavelengths >1670 Å, as suggested by Inn and Heimerl (1971). Dissociation in the height range 0–20 km is primarily due to absorption of radiation in the wavelength band 1975–2075 Å.

The height-integrated rate for photolysis of H_2O in the dry model is small compared with the height-integrated rate for photolysis of HCl. It is consequently difficult to find a balance for H_2O in the dry model. We must choose the parameters in such a way as to minimize production of H_2O at low altitudes. In our judgment, the most uncertain parameters are f_{O_2}, k_{10} and k_{11}, arranged in order of increasing uncertainty. But, the ratio f_{O_2}/k_{10} is fixed by the need to find a balance for CO [see Eq. (25)]. Production of H_2O, as given by (28), varies as $k_{11}f_{O_2}/k_{10}$. It follows that only k_{11} is at our disposal in order to optimize the photochemical solution. We chose $k_{11}=10^{-10}$ cm^3 sec^{-1} for the dry model, a factor of 2 less than the room temperature measurement reported by Hochanadel *et al.* (1972). The discrepancy could reflect an inaccuracy in the laboratory determination of the density of HO_2 and in order to cover this possibility we also adjusted the value of k_9. The value listed in Table 2 was taken from Hochanadel *et al.* In the dry model we took $k_9=3\times10^{-12}$ cm^3 sec^{-1}. Other parameters of the dry model are as listed in Table 2.

Densities for H, O, OH, HO_2 and H_2O_2 computed with the dry model are illustrated in Fig. 2. Densities of CO_2 are also included for comparison. The mixing ratio of O_2 is 9.4×10^{-8}, and the corresponding value for CO is 8.8×10^{-5}. The abundances of O_2 and H_2O_2 are comparable at lower altitudes. The number density of H_2O_2 is 7.4×10^{10} cm^{-3} at $z=0$, which should be compared with number densities of 6.8×10^{12}, 5.1×10^{12} and 6.4×10^{11} cm^{-3} for H_2O, HCl and O_2, respectively.

Rates for some key reactions in the dry model are illustrated in Fig. 3. Molecular oxygen is formed mainly above 18 km, with the major contribution coming from k_2. Dissociation of CO_2 below 18 km is balanced by recombination via the reaction sequence (1). The height-integrated rate for production of O_2 is 3×10^{12} cm^{-2} sec^{-1}, this production being balanced by removal through the reaction sequence (2). The height-integrated rate for production of H_2 is 2.2×10^{11} cm^{-2} sec^{-2} which should be compared with a computed loss rate of 2.3×10^{11} cm^{-2} sec^{-1}. Production of H_2O exceeds removal of H_2O by 1.3×10^{10} cm^{-2} sec^{-1}, and there is a similar small imbalance for CO.

Continuity of species requires upward fluxes of CO_2 and H_2 and corresponding downward fluxes of CO and H_2O. The fluxes of individual species must be equal in magnitude and must have the common numerical value 1.3×10^{10} cm^{-2} sec^{-1}. The downward flux of CO is approximately equal to 0.1% of the total photolytic production of CO. Fluxes of this magnitude are readily transported vertically, provided that the vertical eddy coefficient[1] is greater than about 10^4 cm^2 sec^{-1}. The chemical cycle should be completed in the hot lower

[1] This value was derived under the assumption that the mixing ratio of H_2 was approximately 10^{-7}. Note also, as discussed later, that a consideration of O_2 chemistry reinforces the conclusion that the eddy coefficient must exceed 10^4 cm^2 sec^{-1}.

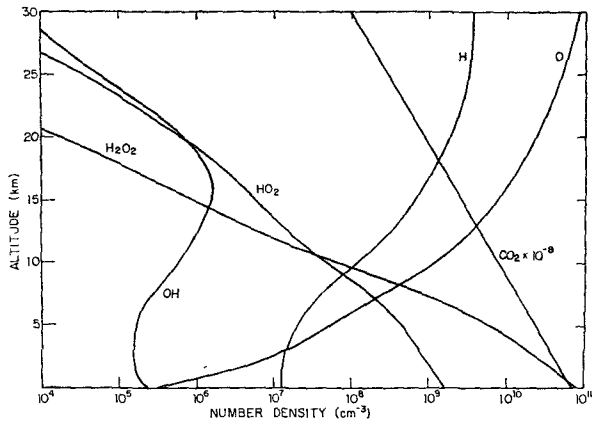

FIG. 2. Concentrations of H, OH, HO_2, H_2O_2, O and CO_2 for the dry model.

atmosphere where there should be efficient conversion of CO and H_2O to CO_2 and H_2 in the global reaction

$$CO+H_2O \rightarrow CO_2+H_2. \quad (29)$$

The time constant associated with (29) can be readily estimated using data presented by Graven and Long (1954). The effective rate constant (cm^3 sec^{-1}) is given approximately by

$$k_{29}=2\times10^2 \exp(-67.3/RT)[CO]^{-\frac{1}{2}}, \quad (30)$$

and the time constant associated with (29) is approximately 2×10^8 sec at the surface of Venus if the mixing ratios of H_2O and CO are taken equal to 8.8×10^{-5}. On the other hand, the time constant associated with the downward flux of CO and H_2O from the upper atmosphere is much longer, approximately 10^{13} sec. It follows that the downward flux should introduce a trivial perturbation to conditions in the lower atmosphere, and the relative concentrations of CO, CO_2, H_2 and H_2O should be consistent with thermodynamic equilibrium.

We can now estimate the mixing ratio of H_2. If we assume that the relative concentrations of CO, CO_2, H_2

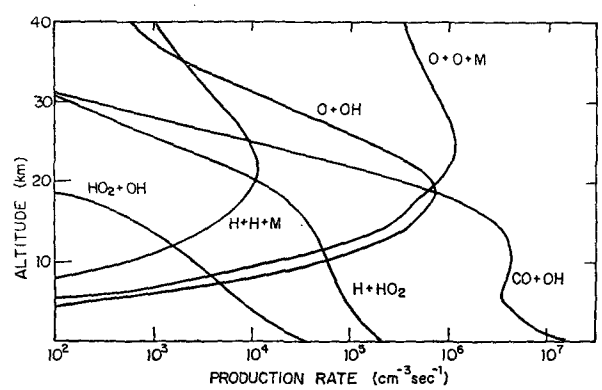

FIG. 3. Production rates for key reactions leading to production of H_2 (H+H+M and H+HO_2), O_2 (O+OH and O+O+M), CO_2 (CO+OH) and H_2O (HO_2+OH), in the dry model.

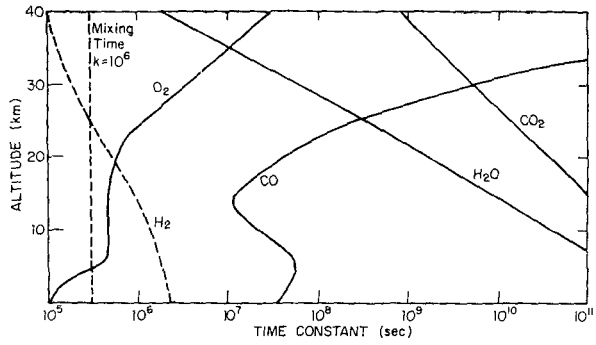

FIG. 4. Time constants in the dry model, for chemical removal of CO, CO_2, H_2 and H_2O. The dynamical time constant for an assumed eddy diffusion coefficient $K=10^6$ cm^2 sec^{-1} is included for comparison.

and H_2O are controlled by (29) and its inverse, then

$$f_{H_2}=Kf_{H_2O}f_{CO}, \tag{31}$$

where K is the appropriate equilibrium constant. Using data presented in the Janaf tables we find

$$f_{H_2}=7\times10^{-8}, \tag{32}$$

if

$$f_{CO}=f_{H_2O}=8.8\times10^{-5}. \tag{33}$$

Chemical time constants for long-lived species (CO, O_2, CO_2, H_2, H_2O) are illustrated in Fig. 4; corresponding data for short-lived species (OH, HO_2, H, O, H_2O_2) are shown in Fig. 5. Fig. 5 also includes time constants for odd H, odd O and free Cl. The various time constants are defined in Appendix B. We note that the assumptions of the present model require that time constants in Fig. 4 must be long compared with time constants for vertical motion. In like manner, time constants in Fig. 5 must be short compared with dynamical times. For reference, we indicate in both Figs. 5 and 6 the dynamical time constants which would apply if vertical motion were characterized by an effective eddy coefficient $K=10^6$ cm^2 sec^{-1}. If the eddy coefficient had this value, then the present analysis would be valid over the height range 5–27 km. Odd hydrogen would be in dynamical equilibrium above 27 km. The distribution of O_2 below 5 km would be determined by a combination of chemistry and dynamics. Some small correction would be required for H, OH and HO_2 above 27 km but the correction would be generally trivial in the present context. The mixing ratio of O_2 would be an increasing function of height between 0 and 5 km, with a mean value of about 10^{-7}. The mixing ratio of O_2 at higher altitudes could be somewhat higher than this value.

If the eddy coefficient were less than 10^6 cm^2 sec^{-1}, a much larger correction would be required for lower altitude O_2. Indeed, as discussed in Appendix C, it would appear that physically acceptable solutions can be obtained only if the eddy coefficient exceeds 4×10^4 cm^2 sec^{-1} over the height range 0–6 km. If the eddy coefficient were larger than 10^6 cm^2 sec^{-1} then O_2 should be well mixed throughout the atmosphere. The concentrations of odd H and odd O would require modification at higher altitudes. Production of O_2 would be reduced, and the recombination path (1) would be relatively more important than (2). The mixing ratio of O_2 would be lowered accordingly.

Computed number densities for H, OH, HO_2, H_2O_2 and O are shown in Fig. 6 for the wet model. The mixing ratios of CO, H_2O, O_2 and HCl are 4.8×10^{-5}, 4.8×10^{-5}, 7×10^{-8} and 8×10^{-7}, respectively. The height-integrated production rates for CO_2, O_2, H_2 and H_2O are, within tolerable limits, equal to the corresponding height integrated loss rates. The production rates are 1.1×10^{13}, 3.2×10^{12}, 2.5×10^{11} and 3.7×10^{10} cm^{-2} sec^{-1} for CO_2, O_2, H_2 and H_2O, respectively. Volume rates for several important reactions are shown in Fig. 7. As in the dry model, O_2 is formed above 18 km by k_2 and k_8, and removed below 5 km by (2). Water is formed at low altitudes by k_{11} and removed at the same rate at high altitudes by J_5. Molecular hydrogen is catalytically removed by Cl and reformed by k_{10} and k_{13}.

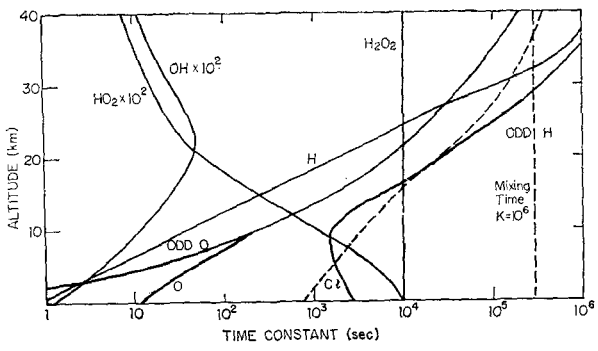

FIG. 5. Time constants in the dry model, for chemical removal of H, OH, HO_2, H_2O_2, O, odd H, free Cl and odd O. The dynamical time constant for an eddy coefficient $K=10^6$ cm^2 sec^{-1} is included for comparison.

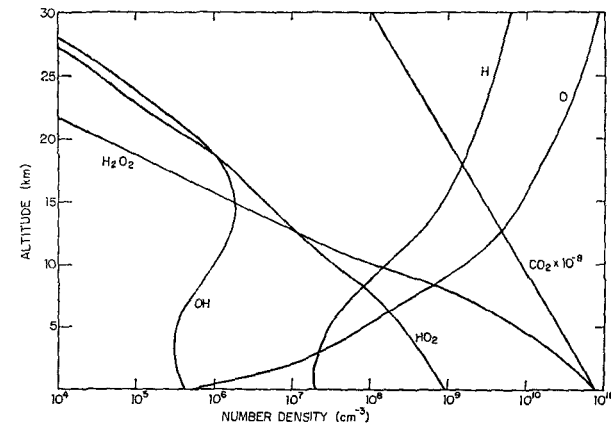

FIG. 6. Concentrations of H, OH, HO_2, H_2O_2, O and CO_2 for the wet model.

Ozone is an exceedingly rare component in both wet and dry models. The column abundance is approximately 10^{-6} cm atm, with a peak concentration of about 3×10^{7} cm^{-3} at 10 km. The predicted concentration of O_3 depends critically on the concentration of O_2 above 10 km. The prediction is thus sensitive to the value of the eddy mixing coefficient at low altitudes. If the eddy coefficient is less than 3×10^{4} cm^2 sec^{-1}, then the concentrations of O_2, and therefore O_3, will be larger than values derived here. The observational upper limit on O_2 reported by Traub and Carleton (1973) could permit O_3 concentrations as large as 10^{-4} cm atm. An observation of O_3 would be valuable, and would provide useful information on the strength of atmospheric mixing in the lower stratosphere and upper troposphere of Venus.

5. Concluding remarks

We have presented a model for the photochemistry of the Venus atmosphere which satisfactorily accounts for the stability of CO_2. The recombination path is similar to that believed appropriate for Mars and is catalyzed by trace hydrogenous species such as H, OH, HO_2 and H_2O_2. Carbon monoxide is removed by

$$CO+OH \rightarrow CO_2+H, \tag{34}$$

with OH formed either by

$$O+HO_2 \rightarrow OH+O_2, \tag{35}$$

or

$$h\nu+H_2O_2 \rightarrow 2OH. \tag{36}$$

We did not explicitly treat possible catalysis of CO_2 recombination by trace quantities of free chlorine. Prinn (1971) suggested that the dominant path for recombination of Venus CO_2 might be

$$Cl+O_2+CO_2 \rightarrow ClOO+CO_2, \tag{37}$$

followed by

$$ClOO+CO \rightarrow ClO+CO_2, \tag{38}$$

and

$$ClO+CO \rightarrow Cl+CO_2. \tag{39}$$

Omission of these reactions in the present context should not be interpreted to reflect a judgment regarding their possible importance. They were omitted primarily due to the lack of relevant laboratory data.[2] Prinn's scheme could be important, however, and would proceed in addition to, but not in competition with, the hydrogenous scheme emphasized here. In particular, our estimates for the mixing ratio of O_2 could be too high if (37)–(39) are found to be important for Venus.

[2] We may note, however, that the reactions $CO+HO_2 \rightarrow CO_2+OH$ and $CO+O_2 \rightarrow CO_2+O$ which are to some extent analogous to (38) are, in fact, negligibly slow at temperatures of interest in the present study. Analogy would support the notion that reactions (37), (39) and (40) should be rapid and suggests that Cl may indeed catalyze recombination of CO and O, if not CO and O_2, in the Venus atmosphere.

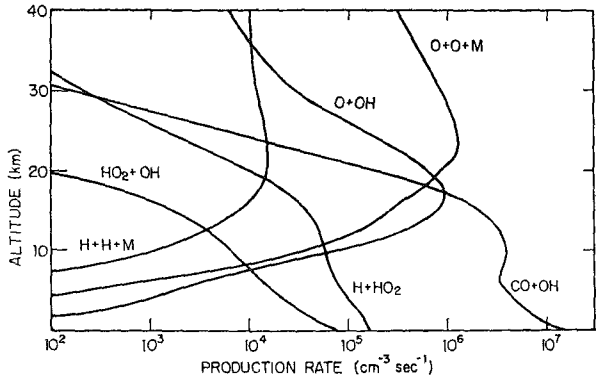

FIG. 7. Production rates (cm^{-3} sec^{-1}) for key reactions leading to production of H_2 (H+H+M and H+HO_2), O_2 (O+OH and O+O+M), CO_2 (CO+OH) and H_2O (HO_2+OH), in the wet model.

Free chlorine can also catalyze recombination of CO and O. The reaction sequence (37) followed by

$$ClOO+O \rightarrow ClO+O_2 \tag{40}$$

and (39) offers a recombination path which could proceed in addition to (1) and which might be important below about 10 km. Some indirect support for (37) and (40) can be obtained from a laboratory study of oxygen recombination in the presence of Cl_2. Kaufman (1958) concluded that his data could be understood if (40) were fast, and if the rate constant for (37) were of order 10^{-31} cm^6 sec^{-1}. There is, however, no direct evidence for the reactions with CO_2 and CO, although other chlorine reactions have been involved in a variety of contexts as discussed by Kaufman (1958). If it turns out that (37), (39) and (40) are indeed important, then densities of atomic oxygen and ozone will be less than values computed in the present paper at altitudes below about 10 km. Other features of the present work would be unaltered, however. In particular, dissociation of CO_2 above 20 km would still be expected to lead mainly to formation of O_2 which must be removed by (2) and its chlorine equivalent (37)–(39).

The mixing ratio of O_2 in the vicinity of the Venus cloud deck must be small, of order 10^{-7} or less. Otherwise, dissociation of HCl and subsequent chemistry would lead to production of unacceptably large quantities of H_2O. Our predictions for O_2 are consistent with the observational limit imposed by Traub and Carleton (1973). We noted, however, that O_2 may not be homogeneously mixed with CO_2 throughout the upper atmosphere of Venus.

The abundance of H_2O in the atmosphere of Venus is uncertain. We argued that H_2O must be at least as abundant as CO in the bulk of the atmosphere and most of the Venus H_2O could be formed as a by-product of upper atmospheric chemistry.

The present work should impose important constraints on attempts to model the chemistry of sulphur in the atmosphere of Venus, a matter of importance in

view of the recent suggestion by Young (1973) regarding the composition of the clouds. The rate for formation of H_2SO_4 may be limited by the available supply of O_2.[3]

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APPENDIX A

The Chemical Model

The detailed chemical model adopted for present purposes is summarized in Table 2. We assume that chemical equilibrium holds for Cl, Cl_2, H, OH, HO_2, H_2O_2 and O. Then

$$J_4[HCl]+2J_7[Cl_2] = 2k_{15}[Cl]^2[CO_2]+k_{14}[Cl][H_2], \quad (A1)$$

$$k_{15}[Cl]^2[CO_2]=J_7[Cl_2], \quad (A2)$$

$$k_5[CO][OH]+k_8[O][OH]+2J_4[HCl]+J_5[H_2O] = k_3[H][O_2][CO_2]+(k_{10}+k_{12})[H][HO_2] +2k_{13}[H]^2[CO_2], \quad (A3)$$

$$2k_9[HO_2]^2+J_5[H_2O]+2k_{12}[H][HO_2]+k_4[O][HO_2] = k_5[CO][OH]+k_{11}[OH][HO_2] +k_8[O][OH], \quad (A4)$$

$$k_3[H][O_2][CO_2] = (k_{10}+k_{12})[H][HO_2]+k_{11}[OH][HO_2] +2k_9[HO_2]^2+k_4[O][HO_2], \quad (A5)$$

$$k_9[HO_2]^2=J_6[H_2O_2], \quad (A6)$$

$$2J_2[O_2]+J_1[CO_2] = 2k_2[O]^2[CO_2]+k_4[O][HO_2]+k_8[O][OH]. \quad (A7)$$

We can combine (A1), (A2) to give (11), where

$$p(HCl)=k_{14}[Cl][H_2]-J_4[HCl]. \quad (A8)$$

Similarly (A3), (A4) and (A5) can be combined to give (9) with

$$p(H_2)=k_{10}[H][HO_2]+k_{13}[H]^2[CO_2] -J_4[HCl], \quad (A9)$$

$$p(H_2O)=k_{11}[OH][HO_2]-J_5[H_2O]. \quad (A10)$$

In like manner (A4) and (A5) imply (10) with

$$p(CO_2)=k_5[CO][OH]-J_1[CO_2], \quad (A11)$$

$$p(O_2)=k_2[O]^2[CO_2]+k_8[O][OH]-k_9[HO_2]^2 -J_2[O_2]-k_{12}[H][HO_2]. \quad (A12)$$

Reactions involving O_3 are generally unimportant for Venus, and have been omitted in Eqs. (A1)–(A11). These reactions were, however, included in the detailed numerical calculations described earlier in this paper. We introduce here a number of additional approximations in order to provide a simple analytic framework for interpretation of the detailed numerical results. Below 6 km the relative concentrations of H, OH and HO_2 are controlled by k_3, k_4, k_5, k_9, k_{12} and J_6. Above 8 km, the relative concentrations of H, OH, HO_2 and O are controlled by k_3, k_4 and k_8.

Below 20 km, we have

$$\frac{[OH]}{[H]}=\frac{k_3[O_2][CO_2]+k_{12}[HO_2]}{k_5[CO]}\approx\frac{k_3[O_2][CO_2]}{k_5[CO]}. \quad (A13)$$

Below 6 km, we have

$$k_{12}[H]+k_4[O]\ll 2k_9[HO_2]. \quad (A14)$$

Thus

$$\frac{[HO_2]^2}{[OH]}\approx\frac{k_5[CO]}{2k_9}. \quad (A15)$$

Above 6 km we have (A14) in the reverse direction and

$$\frac{[HO_2]}{[OH]}\approx\frac{k_5[CO]}{k_{12}[H]+k_4[O]}. \quad (A15')$$

If $k_{11}[OH]/k_{10}[H]\ll 1$, that is, if

$$\frac{f_{O_2}}{f_{CO}}\ll\frac{k_5k_{10}}{k_{11}k_3[CO_2]}, \quad (A16)$$

where $f_{O_2,CO}$ are mixing ratio of O_2 and CO, respectively, then the equation for odd H is simply

$$k_{10}[H][HO_2]\approx J_5[H_2O]+J_4[HCl]. \quad (A17)$$

Expressions (14)–(16) can be readily derived using (A13), (A15) and (A17); expressions (17)–(20), which are appropriate in the height range 6–18 km, can be derived using (A13), (A15′), (A17) and (A7). The bulk of the total CO recombination in the Venus atmosphere

[3] *Note added in proof.* The dry model in this paper requires some net conversion of H_2O to H_2 through the global reaction (6) at the planetary surface. Taking a value 10^{-10} cm^3 sec^{-1} for k_{11} we estimate that the magnitude of the downward flux of H_2O, and consequently the upward flux of H_2, should be 1.3×10^{10} cm^{-2} sec^{-1}. It appears now that this value may be too low. Recent laboratory work by G. A. Takucs and G. P. Glass (*J. Phys. Chem.*, 77, p. 1948) suggests that the reaction

$$OH + HCl \rightarrow H_2O + Cl$$

may provide a significant source of atmospheric H_2O in addition to that derived from

$$OH + HO_2 \rightarrow H_2O + O_2.$$

After including this additional path for H_2O production, we find that the downward flux of H_2O is increased to 6×10^{10} cm^{-2} sec^{-1}. Other features of the dry model remain essentially unchanged. A balance can be obtained in the wet model, allowing for the new source of H_2O, if we take the mixing ratios of CO, O_2, H_2O and HCl as 7.8×10^{-5}, 5.0×10^{-8}, 1.8×10^{-4} and 9×10^{-7}, respectively.

occurs below 18 km and is satisfactorily approximated by (26) and (27). Note that recombination of CO below 20 km is essentially independent of the value for the mixing ratio of CO.

We consider now the alternate case in which H recombination leads to production of H_2O. In this case we have

$$k_{11}k_3f_{O_2}[CO_2] \gg k_5k_{10}f_{CO}. \tag{A22}$$

As before, the expressions for [H], [OH] and $[HO_2]$ assume different limiting forms depending on whether HO_2 is cycled by k_7 or k_4+k_{12}. In the first case we have

$$[HO_2]=\left\{\frac{k_5[CO](J_5[H_2O]+J_4[HCl])}{2k_9k_{11}}\right\}^{\frac{1}{3}}, \tag{A23}$$

$$[H]=\frac{2^{\frac{1}{3}}k_9^{\frac{1}{3}}k_5^{\frac{2}{3}}[CO]^{\frac{2}{3}}(J_5[H_2O]+J_4[HCl])^{\frac{2}{3}}}{k_{11}^{\frac{2}{3}}k_3[O_2][CO_2]}, \tag{A24}$$

$$[OH]=\frac{2^{\frac{1}{3}}k_9^{\frac{1}{3}}(J_5[H_2O+J_4[HCl])^{\frac{2}{3}}}{k_{11}^{\frac{2}{3}}k_5^{\frac{1}{3}}[CO]^{\frac{1}{3}}}. \tag{A25}$$

In the second case

$$[HO_2]=\frac{k_5[CO]\{J_4[HCl]+J_5[H_2O]\}}{k_{11}J_1[CO_2]}, \tag{A26}$$

$$[H]=\frac{J_1[CO_2]}{k_3[O_2][CO_2]}, \tag{A27}$$

$$[OH]=\frac{J_1[CO_2]}{k_5[CO]}, \tag{A28}$$

$$[O]=\frac{k_{11}\{J_1[CO_2]\}^2}{k_4k_5[CO]\{J_4[HCl]+J_5[H_2O]\}}. \tag{A29}$$

As before, (A23)–(A25) are valid mainly below 6 km and (A26)–(A29) apply between 6 km and 18 km. The corresponding expressions for the CO recombination rate are

$$R(CO)=2^{\frac{1}{3}}k_5^{\frac{2}{3}}k_9^{\frac{1}{3}}k_{11}^{-\frac{2}{3}}[CO]^{\frac{2}{3}}(J_5[H_2O]+J_4[HCl])^{\frac{2}{3}}, \tag{A30}$$

$$R(CO)=J_1[CO_2]. \tag{A30'}$$

Above 20 km, $k_5[CO] \ll k_8[O]$, and the relative concentrations of H, OH and HO_2 are controlled by k_3, k_4 and k_8. Then

$$\frac{[OH]}{[H]}=\frac{k_3[O_2][CO_2]}{k_8[O]}, \tag{A31}$$

$$\frac{[OH]}{[HO_2]}=\frac{k_4}{k_8}, \tag{A32}$$

and

$$k_{13}[H]^2[CO_2] \approx J_4[HCl]+J_5[H_2O]. \tag{A33}$$

The photochemical equations can now be solved to give the approximate results given by (21)–(24) which are identical in both wet and dry models.

The rate for recombination of CO is given by (27) and

$$R(O_2) \approx \tfrac{1}{2}J_1[CO_2]. \tag{A34}$$

APPENDIX B

Time Constants

The time constants for CO_2, CO, H_2O, O, H, OH, HO_2 and H_2O_2 can be calculated in the usual way. The time constants for O_2, H_2, odd O, odd H and Cl are calculated from the following expressions:

$$\tau_{O_2}=\frac{[O_2]}{k_9[HO_2]^2+k_{12}[H][HO_2]} \tag{B1}$$

$$\tau_{H_2}=\frac{[H_2]}{J_4[HCl]} \tag{B2}$$

$$\tau_{\text{odd O}}=\frac{[O]+[OH]}{2k_2[O]^2[CO_2]+k_5[OH][CO]+2k_8[OH][O]+k_{11}[OH][HO_2]} \tag{B3}$$

$$\tau_{\text{odd H}}=\frac{[H]+[OH]+[HO_2]}{2k_{10}[H][HO_2]+2k_{11}[OH][HO_2]+2k_{13}[H]^2[CO_2]} \tag{B4}$$

$$\tau_{Cl}=\frac{1}{k_{14}[H_2]}. \tag{B5}$$

In these calculations f_{H_2} is taken to be 7.5×10^{-8} as estimated from thermodynamic equilibrium on the surface of Venus.

APPENDIX C

Molecular Oxygen

The concentration of O_2 is given by

$$\frac{d\phi}{dz} = p - Ln, \tag{C1}$$

$$\phi = -K\left(\frac{dn}{dz} + \frac{n}{T}\frac{dT}{dz} + \frac{n}{H_{av}}\right), \tag{C2}$$

where ϕ, n are the flux and number density of O_2.

In order to analytically approximate the solution we take

$$\left.\begin{aligned} p &= 0 \\ L = \tau_c^{-1} &= 5\times10^{-6}\ \text{sec}^{-1} \end{aligned}\right\}, \tag{C3}$$

where τ_c is the mean chemical time constant for O_2 in the height range 0–6 km where O_2 may not be well mixed. Little error is introduced by this procedure.

The boundary conditions appropriate for the present context are

$$\left.\begin{aligned} \phi(z=6\ \text{km}) &= -3\times10^{12}\ \text{cm}^{-2}\ \text{sec}^{-1} \\ n(z=0\ \text{km}) &= 10^{-7}\times[CO_2] \end{aligned}\right\}. \tag{C4}$$

The condition on ϕ is set by the column production rate of O_2 above 18 km. The condition on n is set by the requirement that we should have an overall balance for various species. Solutions for various K are shown in Fig. 8. Acceptable solutions must have $\phi<0$ or $df_{O_2}/dz>0$ over the height range of interest. It follows that consistent O_2 profiles are obtained only for $K>4\times10^4$ cm^2 sec^{-1}.

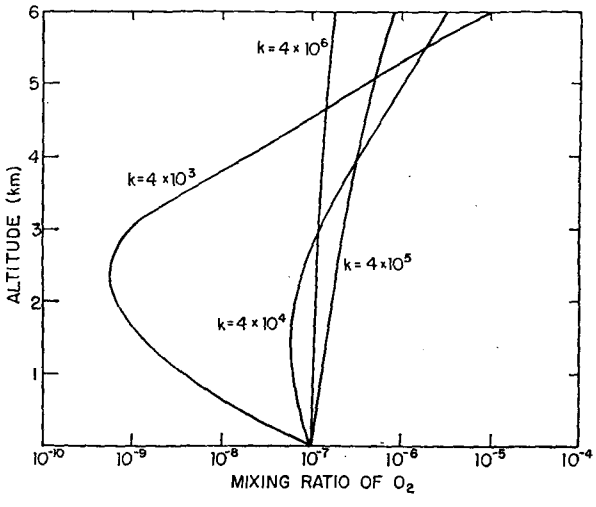

FIG. 8. Mixing ratios of O_2 for various eddy coefficients.

REFERENCES

Avduevsky, V. S., M. Ya. Marov and M. K. Rozhdestvensky, 1970: A tentative model of the Venus atmosphere based on the measurements of Veneras 5 and 6. *J. Atmos. Sci.*, **27**, 561–568.

Bader, L. W., and E. A. Ogryzlo, 1964: Recombination of chlorine atoms. *Nature*, **201**, 491–492.

Baulch, D. L., D. D. Drysdale and A. C. Lloyd, 1969: *High Temperature Reaction Rate Data*, 3, 18.

Berge, G. L., and E. W. Greisen, 1969: High-resolution interferometry of Venus at 3.12 cm wavelength. *Astrophys. J.*, **156**, 1125–1134.

Brinkmann, R. T., A. E. S. Green and C. A. Barth, 1966: A digitalized solar ultraviolet spectrum. NASA Tech. Rept. 32–951.

Connes, P., J. Connes, W. S. Benedict and L. D. Kaplan, 1967: Traces of HCl and HF in the atmosphere of Venus. *Astrophys. J.*, **147**, 1230–1237.

Dainton, F. S., and P. B. Ayscough, 1967: *Gaseous Photochlorination: Photochemistry and Reaction Kinetics*. Cambridge University Press, 64–92.

Detwiler, C. R., D. L. Garett, J. D. Purcell and R. Tousey, 1961: The intensity distribution in the ultraviolet solar spectrum. *Ann. Géophys.*, **17**, 9–18.

Fink, U., H. P. Larsen, G. P. Kuiper and R. F. Poppen, 1972: Water vapor in the atmosphere of Venus. *Icarus*, **17**, 617–631.

Graven, W. M., and F. J. Long, 1954: Kinetics and mechanism of the two opposing reactions of the equilibrium $CO+H_2O=CO_2+H_2$. *J. Amer. Chem. Soc.*, **76**, 2602–2607.

Handbook of Geophysics and Space Environments, S. L. Valley, Ed., 1965: Air Force Cambridge Research Laboratory.

Hochanadel, C. J., J. A. Ghormley and P. J. Orgren, 1972: Absorption spectrum and reaction kinetics of the HO_2 radical in the gas phase. *J. Chem. Phys.*, **56**, 4426–4432.

Inn, E. C. Y., and J. M. Heimerl, 1971: The photolysis of CO_2 at wavelengths exceeding 1740 Å. *J. Atmos. Sci.*, **28**, 838–841.

Janaf Thermodynamical Tables, 1965: Compiled by Dow Chemical Co., Midland, Mich., under PB-168370 (Clearinghouse for Federal Scientific and Technical Information).

Janssen, M. A., R. E. Hills, D. C. Thorton and W. J. Welch, 1973: Venus: New microwave measurements show no atmospheric water vapor. *Science*, **179**, 994–996.

Kaufman, F., 1958: The air afterglow and its uses in the study of some reactions of atomic oxygen. *Proc. Roy. Soc. London*, **A247**, 123–139.

——, 1964: Aeronomic reactions involving hydrogen: A review of recent laboratory studies. *Ann. Géophys.*, **20**, 106–114.

——, 1969: Elementary gas reactions. *Annual Reviews of Physical Chemistry*, Vol. 20, Annual Reviews, Inc., Palo Alto, 45–90.

Larkin, F. S., and B. A. Thrush, 1964: Recombination of hydrogen atoms in the presence of atmospheric gas. *Disc. Faraday Soc.*, **37**, 112–117.

McElroy, M. B., and T. M. Donahue, 1972: Stability of the Martian atmosphere. *Science*, **177**, 986–988.

NASA, 1972: Pioneer Venus. Report of a study by the Science Steering Group.

Parkinson, T. D., and D. M. Hunten, 1972: Spectroscopy and aeronomy of O_2 on Mars. *J. Atmos. Sci.*, **29**, 1380–1390.

Prinn, R. G., 1971: Photochemistry of HCl and other minor constituents in the atmosphere of Venus. *J. Atmos. Sci.*, **28**, 1058–1068.

Reeves, R. R., G. Manella and P. Harteck, 1960: Rate of recombination of oxygen atoms. *J. Chem. Phys.*, **32**, 632–633.

Rogers, A. E. E., R. P. Ingalls and L. P. Rainville, 1972: The topography of a swath around the equator from the wavelength dependence of the radar cross section. *Astron. J.*, **77**, 100–103.

Romand, J., and B. Vodar, 1948: Spectre d'absorption de l'acide chlorhydrique gazeaux dans la région de Schumann. *Compt. Rend.*, **226**, 238–240.

Schofield, K., 1967: An evaluation of kinetic rate data for reactions of neutrals of atmospheric interest. *Planetary Space Sci.*, **15**, 643–670.

Schultz, E. D., and A. C. Holland, 1963: The solar flux incident at the top of the atmospheres of earth and neighboring planets for the spectral range 50 Å to 3000 Å. NASA CR-11, Washington, D. C.

Seery, D. J., and D. Britton, 1964: The continuous absorption spectra of Cl_2, Br_2, BrCl, ICL and IBr. *J. Phys. Chem.*, **68**, 2263–2266.

Shemansky, D. E., 1972: CO_2 extinction coefficient 1700–3000 Å. *J. Chem. Phys.*, **56**, 1582–1587.

Simonaites, R., and J. Heicklen, 1972: Kinetics and mechanisms of the reaction of $O(^3P)$ with carbon monoxide. *J. Chem. Phys.*, **56**, 2004–2011.

Sinclair, A. C. E., J. P. Basart, D. Buhl and W. A. Gale, 1972: Precision interferometric observations of Venus at 11.1 cm wavelength. *Astrophys. J.*, **175**, 555–572.

Thompson, B. A., P. Harteck and R. R. Reeves, 1963: Ultraviolet absorption coefficients of CO_2, CO, O_2, H_2O, N_2O, NH_3, NO, SO_2, and CH_4 between 1850 and 4000 Å. *J. Geophys. Res.*, **68**, 6431–6436.

Traub, W. A., and N. P. Carleton, 1973: A search for H_2O and O_2 on Venus. Paper presented at American Astronomical Society Third Annual Meeting, Tucson, Ariz.

Vinogradov, A. P., Yu. A., Surkov, B. M. Andreichikov, O. M. Kalinkina and I. M. Grechishera, 1971. The chemical composition of the atmosphere of Venus. *Planetary Atmospheres*, C. Sagan, T. C. Owen and H. J. Smith, Eds., Reidel, Holland, 3–16.

Westenberg, A. A., and N. deHass, 1968: Atom-molecule kinetics using ESR detection IV. Results for $Cl+H_2 \rightleftarrows HCl+H$ in both directions. *J. Chem. Phys.*, **48**, 4405–4415.

Widing, K. G., J. D. Purcell and G. D. Sandlin, 1970: The UV continuum 1450–2100 Å and the problem of the solar temperature minimum. *Solar Phys.*, **12**, 52–62.

Young, A. T., 1973: Are the clouds of Venus sulphuric acid? *Icarus*, **18**, 564–582.

Young, L. D. G., 1972: High resolution spectra of Venus—A review. *Icarus*, **17**, 632–658.